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Thermal and Morphological Properties of Polyurethane Foams Prepared from Microwave-assisted Glycolyzed Products of PET Bottles Wastes

Chutima Aiemsa-art[a,b], Prompoom Phanwiroj[a,b] and Pranut Potiyaraj[a,b*]

[a]*Center of Excellence in Textiles, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[b]*Center for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand*

Abstract

Polyethylene terephthalate (PET) waste from post-consumer soft drink bottles was depolymerized under microwave energy instead of conventional heating with diethylene glycol (DEG) at the molar ratio between PET and DEG of 1:4 in a modified domestic microwave oven at the irradiation power of 600 W. Zinc acetate, sodium carbonate and sodium bicarbonate were used as a catalyst at 0.5% by weight of PET. It was reported that replacement of conventional heating with microwave energy shortened the chemical reaction time significantly. Polyurethane foams were then successfully prepared from the glycolyzed products by reacting them with polymeric diphenylmethane diisocyanate and polyethylene glycol as a chain extender. Thermal and morphological properties of the prepared polyurethane foams were then studied. It was found that the thermal behavior of the prepared foams was similar while their morphology was affected by the catalyst used. The most uniform cell structure was observed when the glycolyzed product that used sodium bicarbonate as a catalyst was used to prepare polyurethane foam.

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Keywords: microwave; polyethylene terephthalate; polyurethane; recycle

1. Introduction

Due to its superior mechanical and physical properties, polyethylene terephalate (PET) is one of the most versatile commodity thermoplastics widely used in a broad range of applications, particularly in

* Corresponding author. Tel.: +66-2218-5544; fax: +66-2218-5561.
E-mail address: pranut.p@chula.ac.th.

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textiles and packaging. As a result of its high consuming volume, a large amount of PET wastes is inevitably generated, including polymer manufacturing wastes as well as the products after the end of their useful life. Post-consumer soft drink bottles are one of the main sources of PET wastes. Therefore, several researchers have been focused on finding a simple economic route to recycle PET wastes. In general, PET wastes can be recycled either physically or chemically. Chemical recycling through depolymerization of PET wastes leads to the formation of monomer or oligomers which can be used for synthesizing a new material with desired properties.

Chemical processes applied in polymer recycling are divided into glycolysis, hydrolysis, methanolysis, aminolysis and other methods. Among these techniques, the glycolysis process has been studied extensively because it is possible to conduct the reaction using safe and economical reactants under lower temperatures and pressures, in contrast with other process such as supercritical methanol, while hydrolysis under acidic or basic condition may cause corrosion and pollution problems [1], [2]. There have been reported that products obtained by glycolysis of PET were employed to prepare unsaturated polyester resins, urethane oils and polyurethanes [3–5]. However, the time need to complete the glycolysis reaction conducted under conventional heating sources can be as long as 4 to 6 hours [2], [6] – [7]. The inefficiency in term of energy complicates the commercial application of this recycling technique.

The use of microwave energy as a replacement of conventional thermal heating source in chemical reaction has received much attention in recent years due to the significantly decrease of reaction time while retaining, or even increasing, the reaction yields [8]. In order to improve energy efficiency, microwave energy can also be used for glycolysis of PET wastes. It was reported that the time needed to complete the glycolysis reaction, when microwave radiation was used as a replacement of conventional thermal heating source, was shortened down to 6 – 10 min [9], [10].

The aim of the present study is to investigate thermal and morphological properties of polyurethane foam prepared from microwave-assisted glycolyzed products of PET wastes. Post-consumer PET soft drink bottles were depolymerized by glycolysis with diethylene glycol (DEG) in the presence of different catalysts under microwave radiation in place of conventional heating. The microwave-assisted glycolyzed products were then reacted with diphenylmethane diisocyanate (MDI) to synthesize polyurethane foams. The thermal and morphological properties of the prepared polyurethane foams were investigated.

2. Experimental

2.1. Chemicals and materials

Post-consumer PET soft drink bottles were procured from a local market. The bottles after removing labels and caps were cleaned, dried and chopped into flakes. PET flakes were pulverized into fine particles with a particle size of less than 1.0 mm. Diethylene glycol (DEG), which used as a glycol in the depolymerization reaction, was purchased from Ajax Finechem. Zinc acetate ($Zn(Ac)_2$), sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) were used as a catalyst. These catalysts were obtained from Fluka. Polymeric diphenylmethane diisocyanate (PMDI) with isocyanate content of 29.2 wt.% were kindly supplied by Siam Chemical Industry (Samut Prakan, Thailand). Polyethylene glycol which has the molecular weight of 4000 (PEG4000) purchased from Ajax Finechem was used as a chain extender. All chemicals were of laboratory grade and used without further purification.

2.2. Glycolysis of PET wastes

Grounded PET waste was reacted with DEG at the molar ratio between PET and DEG of 1:4 in the presence of a catalyst. Different catalysts, namely zinc acetate, sodium carbonate and sodium bicarbonate were used at 0.5% by weight of PET. The glycolysis reaction was carried out in 600 W in an LG domestic microwave oven that modified to equip with a reflux condenser on the topside. The glycolysis reaction proceeded for time periods up to 9 min. At the end of the reaction, the mixture was left to cool down until the room temperature was reached and the glycolyzed product was then obtained.

The glycolyzed products were analyzed by a Thermo Scientific Nicolet 6700 Fourier transform infrared spectrometer (FT-IR, Waltham, MA). The spectra were recorded at a frequency range of 400 – 4000 cm^{-1}, a nominal resolution of 4 cm^{-1} with 64 scans. The molecular weight of the glycolyzed products was investigated by a gel permeation chromatography system (GPC, Shimadzu, Tokyo, Japan) using monodisperse polystyrene as the reference and HPLC-grade tetrahydrofuran (THF) as the solvent at the flow rate of carrier solvent of 1.00 ml/min. The hydroxyl value of glycolyzed product was determined according to ASTM D4274-99 Method C. The viscosity was determined using a Brookfield viscometer (Model RTV, Stoughton, MA).

2.3. Synthesis of polyurethane foams

Predetermined amounts of the glycolyzed products and a chain extender (PEG4000) were mixed in a plastic mold and then heated for 10 min on a water bath to maintain the temperature around 80 – 90 oC. After stirring with a mechanical stirrer at 1000 rpm for 1 min, the mixture was cooled down to room temperature. Water as the foaming agent was added, and the whole mixture was stirred vigorously for 1 min. After that PMDI was added and stirred vigorously for 2 min at the amount of PMDI which was calculated in accordance with the hydroxyl values of the glycolyzed products and the chain extender. Polyurethane foams were then finally obtained.

The prepared polyurethane foams were also analyzed by a Thermo Scientific Nicolet 6700 Fourier transform infrared spectrometer (FT-IR, Waltham, MA) at a frequency range of 400 – 4000 cm-1. The thermal stability of the polyurethane foam was studied by a Mettler Toledo TGA/SDTA 851e thermogravimetric analyzer (TGA, Columbus, OH) from 50 to 1,000 oC at a heating rate of 20 oC/min under nitrogen atmosphere. The morphological properties of the obtained polyurethane foams was examined using a Scanning Electron Microscope (SEM, JEOL JSM-5800LV, Tokyo, Japan) at a voltage of 15 kV.

3. Results and Discussion

3.1. Characterization of the glycolyzed products

PET waste was glycolyzed at constant microwave power of 600 W. PET depolymerization was completed within 6, 7 and 9 min when zinc acetate, sodium bicarbonate and sodium carbonate were used as catalyst, respectively. The used of microwave radiation as the energy source in PET glycolysis resulted in the substantial shorter reaction times needed for complete PET degradation compared with conventional heating methods.

The hydroxyl value, viscosity, average molecular weight and molecular weight distributions of the glycolyzed products with different catalysts are presented in Table 1. The results show similar trend to the previous report [11] in term of depolymerization efficiency. Zinc acetate gave the highest reaction rate

indicated that the glycolysis occurred much more rigorously. However, polydispersity index indicated that the glycolyzed products which used sodium bicarbonate possessed more uniform molecules than the others. Surprisingly, the hydroxyl value of the glycolyzed products prepared using zinc acetate as a catalyst was smaller than that using other catalysts. It is possible that the high efficiency of zinc acetate led to molecular degradation other than glycolysis reaction.

Table 1. Hydroxyl value, average molecular weights, molecular weight distributions, and viscosity of the glycolyzed products.

Catalyst used	$\overline{M}_n$	$\overline{M}_w$	Polydispersity Index	Hydroxyl value (mg KOH/g)	Viscosity (cPs)
$Zn(Ac)_2$	965	1131	1.172	570	112
$NaHCO_3$	967	1131	1.169	660	114
Na_2CO_3	971	1139	1.173	600	112

The FTIR spectra of the glycolyzed products that obtained from glycolysis reaction of PET waste using DEG in the presence of different catalysts (zinc acetate, sodium carbonate and sodium bicarbonate) are shown in Fig 1. It can be clearly seen that spectrograph shows -OH band range at 3200 – 3600 cm^{-1} and 1128 cm^{-1} and aromatic C–H at 1504 – 1406 cm^{-1}. The presence of peaks at 1720 cm^{-1} indicates C=O stretching while peaks related to alkyl and C–H appear at 3000 – 2800 cm^{-1}. These absorption peaks imply that the glycolyzed are compounds having hydroxyl and ester groups.

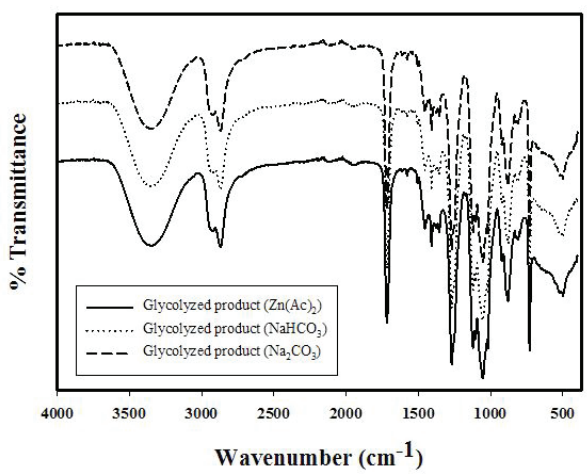


Fig. 1. FT-IR spectra of the glycolyzed products.

3.2. Characterization of polyurethane foams

The FTIR spectra of the polyurethane foams prepared from the glycolyzed products are shown in Fig 2. The spectra exhibit the characteristic peak at 3200 – 3400 cm^{-1} of -NH stretching. The peak at 1720 cm^{-1} indicates C=O of urethane while -NH bending is identified with the peak at 1510 cm^{-1}. The presence of these peaks was attributed to the urethane linkage formation through the reaction between PMDI and the hydroxyl groups of glycolyzed products and/or chain extender.

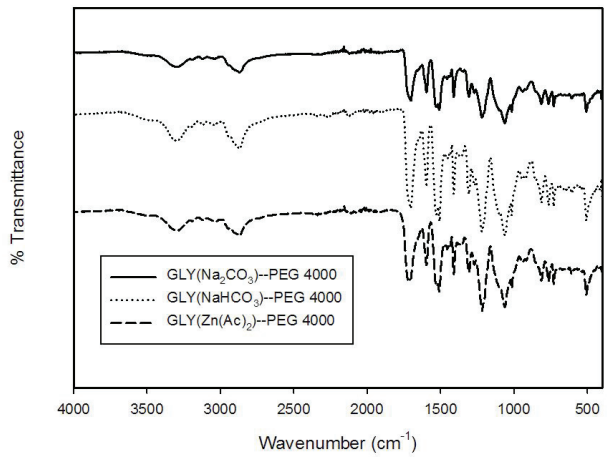


Fig. 2. FT-IR spectra of the prepared polyurethane foams.

Figure 3 shows TGA thermograms of polyurethane foams prepared from various glycolyzed products. It can be seen that all samples showed the same first onset degradation at about 260 °C, the second degradation temperature at about 370 °C, and the final degradation temperature around 590 °C. A similar thermal behavior was observed for all samples.

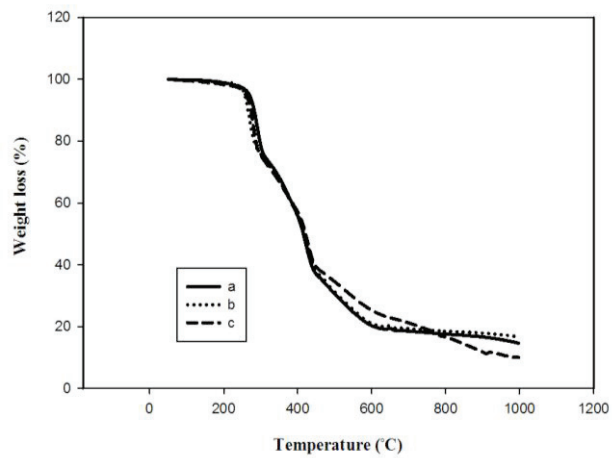
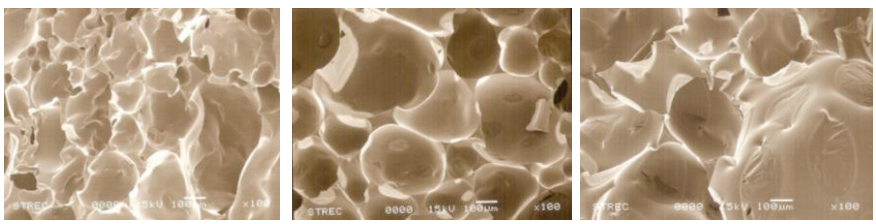


Fig . 3. TGA thermogram of polyurethane foams prepared from glycolyzed products using (a) zinc acetate, (b) sodium bicarbonate, and (c) sodium carbonate as a catalyst.

SEM micrographs of polyurethane foams prepared from different glycolyzed products are exhibited in Fig 4. It can be observed that all polyurethane foam samples have the closed-cell structure.

The cell size of polyurethane foam prepared from glycolyzed products which used zinc acetate as a catalyst was smaller than that of polyurethane foams prepared from sodium bicarbonate and sodium carbonate. This is likely due to the fact that zinc acetate promotes the glycolysis much more rigorous than the other catalyst thus the obtained monomers and/or oligomers are much smaller. The rigorous reaction

also leads to less uniformity of molecular weight distribution thus the cell distribution of foam prepared from glycolyzed products which used zinc acetate as a catalyst was less uniform than that of polyurethane foams prepared from sodium bicarbonate and sodium carbonate. As the average molecular weight of glycolyzed product which used sodium carbonate as a catalyst was higher than that of glycolyzed product which used sodium bicarbonate as a catalyst, thus the cell size of foam prepared from glycolyzed product which used sodium carbonate as a catalyst was larger than that of foam prepared from glycolyzed product which used sodium bicarbonate as a catalyst.



(a) (b) (c)

Fig. 4. SEM micrographs of the prepared polyurethane foams prepared from glycolyzed products which used (a) zinc acetate, (b) sodium bicarbonate, and (c) sodium carbonate as a catalyst.

4. Conclusion

PET bottles were depolymerized by glycolysis in excess of diethylene glycol (DEG) with the presence of different catalysts, i.e. zinc acetate, sodium bicarbonate, and sodium carbonate, under microwave energy. The obtained glycolyzed products were then characterized. In order to prepare polyurethane foams, the glycolyzed products were reacted with PMDI. PEG as a chain extender was also incorporated. The obtained polyurethane foams were investigated for their thermal and morphological characteristics. It was found that all foam samples exhibited similar thermal behaviors as their degradation temperatures were almost the same. All foams also showed the closed-cell structure. However, the profound effect of catalyst used in the glycolysis reaction was reflected on the morphological properties of prepared foams. It was found that polyurethane foam prepared from glycolyzed product which used sodium bicarbonate as a catalyst showed the most uniform cell distribution.

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